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Huge enhancement of the quadratic nonlinear optical susceptibility in push–pull chromophores based on bridged dithienylethylene spacers

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Replacement of the open chain dithienylethylene π-conjugating spacer by its bridged analog in push–pull NLO-phores produces a dramatic increase of the quadratic hyperpolarisability.

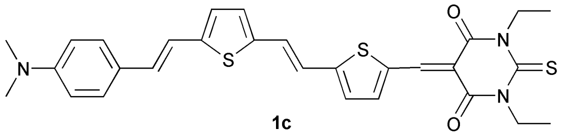
Chromophores for 2nd order nonlinear optics consist of electron-donor and electron-acceptor groups interacting through a π-conjugating spacer.[1] Whereas the optimization of the donor[2] and acceptor[3] groups has led to considerable progress in the synthesis of stable and efficient systems, the relationship between the structure of the conjugating spacer and 2nd order nonlinearity are less clearly understood. Push–pull polyenes can reach huge nonlinearities,[2a,4] but their practical use might be limited by stability problems.

As shown in recent work, thiophene-based spacers lead to stable NLO-phores with second order hyperpolarisabilities sometimes exceeding $10\,000 \times 10^{-48}$ esu.[2b–d,3] These high performances can be related to the moderate resonance energy of thiophene which allows a better π-electron delocalization than *e.g.* benzene-containing spacers.

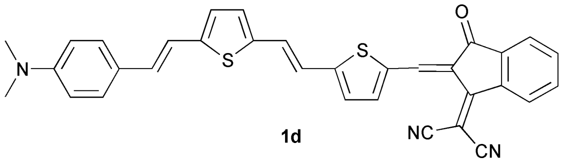
It has been shown that the static hyperpolarizability is correlated with the ground state polarization which is in turn reflected by bond length alternation (BLA).[5] Optimal β values, predicted for BLA intermediate between those for unsubstituted polyenes (~0.10 Å) and the cyanine limit (0.00 Å), have been approached by selecting appropriate combinations of donor and acceptor groups in order to tune the balance between the neutral and charge-separated limiting resonance forms.[4,5]

Previous theoretical and experimental work has shown that the covalent bridging of dithienylethylene (DTE) results in a 0.40 eV decrease of the HOMO–LUMO gap due to a reduction of BLA.[6] On this basis, replacement of DTE by a bridged analog with inherently reduced BLA, can be expected to improve the quadratic hyperpolarizability of the derived push–pull chromophores. In this context, we report here preliminary results on two series of NLO-phores derived from open chain (**1c–e**) and bridged (**2**,**3**) DTE spacers, used in conjunction with *N*,*N*-dialkylaniline donors, and various acceptors.

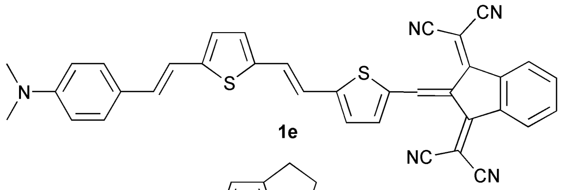
All NLO-phores have been prepared according to the general procedure shown in Scheme 1. DTE **1f** and its bridged analog **2f**[6c] were converted into aldehydes **1g** and **2g** by Vilsmeier formylation. Wittig olefination of **1g** and **2g** with phosphonium iodides bearing the *N*,*N*-dialkylaniline group led to compounds **1h–3h** as a mixture of *E* and *Z* isomers. After separation of the *Z*-isomer, a second formylation led to aldehydes **1i–3i** and the target molecules were obtained by Knoevenagel condensation between **1i**, **2i** and **3i** and various acceptors with active methylene groups. All final compounds have been fully characterized by ^{1}H and ^{13}C NMR, mass spectroscopy and elemental analysis.



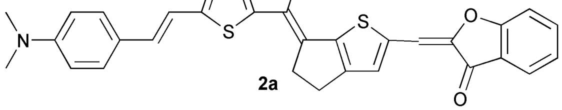
1c



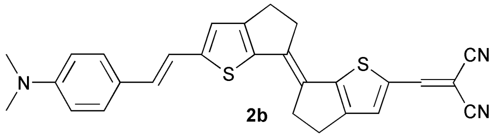
1d



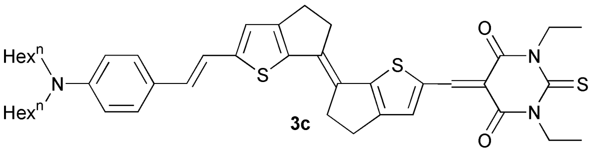
1e



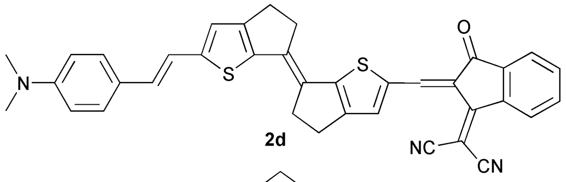
2a



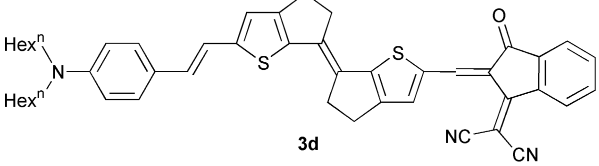
2b



3c



2d



3d

Table 1 lists the UV-vis absorption maxima ($\lambda_{\max}$), second order nonlinear hyperpolarizabilities ($\beta\mu$), and decomposition temperatures (*T*d) of the NLO-phores. Comparison of the data for the open chain and bridged compounds containing similar donor–acceptor pairs shows that the bridging of the spacer produces a considerable red shift of $\lambda_{\max}$, (up to 100 nm between **1d** and **2d**), indicating an enhancement of the effective conjugation. Preliminary tests on **1e** and **2d** gave anomalously low μβ values which were attributed to the poor solubility of the

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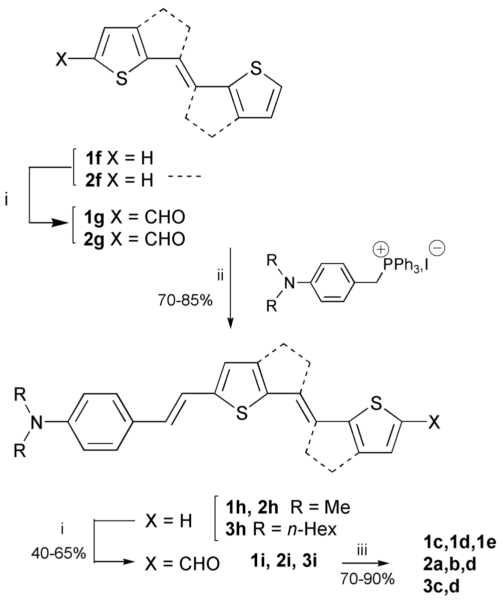

Scheme 1 *Reagents and conditions* (i) $POCl_3$/DMF; (ii) *t*-BuOK/MeCN-THF; (iii) **2b**, malononitrile, $Et_3N/CHCl_3$, rflx 12 h; **2a**, coumaranone, $Al_2O_3/CHCl_3$, room temp, 48 h; **1c**, **3**, thiobarbituric acid, Ac_2O, rflx 2 h; **1d**, **2d**, **3d**, dicyanovinylindan-3-one, EtOH rflx 10 h; Ac_2O, 60 °C 1 h; **1e**, bisdicyanovinylindane, Ac_2O, rflx 1 h.

Table 1 Absorption maxima, quadratic hyperpolarisabilities and decomposition temperatures of chromophores **1**–**3**

Compound	λ_{max}/nm^a	$\mu\beta/10^{-48}$ esu^b	Td/°C^c
1c	606	2720 (1450)	235
1d	656	7100 (3300)	256
1e	720	Nd	250
2a	592	2500 (1500)	300
2b	614	3100 (1600)	308
3c	682	10400 (4400)	235
2d	756	Nd	258
3d	768	19400 (5680)	245

[a] In CH_2Cl_2. [b] Measured in $CHCl_3$ at 1.9 μm by EFISH, values in parentheses represent the zero-frequency hyperpolarizability product $\mu\beta_0$. [c] Determined by differential scanning calorimetry at a rate of 10 °C min^{-1}.

compounds. This problem was resolved by replacing methyl by hexyl groups in compounds **3c** and **3d**.

Comparison of the data for the two series of compounds shows that, for a given acceptor, the bridging of the DTE spacer produces a huge enhancement of μβ which increases from 2720 to 10 400 × 10^{-48} esu for the **1c**/**3c** pair, while for the **1d**/**3d** one, μβ increases by a factor of three and reaches a value of 19 400 × 10^{-48} esu. To the best of our knowledge, this value is the largest ever reported for a NLO-phore based on an heteroaromatic spacer.

Improved thermal stability has already been reported for NLO-phores based on configuration-locked olefinic spacers,[7] or for bridged dithienyl hexatrienes.[8] While the various acceptor groups used here make it difficult to evaluate the specific effect of the spacer on the stability, the similarity of the Td values for open chain and bridged compounds bearing the same acceptor *e.g.* **1d** and **2d** suggests that, in that case, the stability is limited by that of the acceptor. Further support for this hypothesis is provided by the identical *T*d values (235 °C) found for **3c**, **1c** and its analog containing the more stable diphenylamino substituted thiophene donor.[2d] On the other hand, the high Td values for **2a** and **2b** ($\geqslant$ 300 °C) definitively show that thermally stable chromophores can be synthesized from bridged DTE spacers.

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